Molecular and Stable Isotopic Compositions in Delhi Aerosols: Important Contribution from Field Burning of Agricultural Residues

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The city of Delhi experiences severe haze episodes during the winter season, especially in October and November every year, owing to the emissions from local sources (agricultural residue burning) in the neighbouring states, meteorological parameters and secondary particle formation processes in the atmosphere. The present study represents, for the first time, the temporal distributions of organic, inorganic and isotopic characteristics of day-time (divided into three periods) ambient aerosols from the city during high pollution event influenced by agricultural residue burning from neighbouring regions from 8th November to 17th November 2019. The $PM_{2.5}$ samples (n=29) were collected on the rooftop of CSIR-National Physical Laboratory using air sampler. Three samples of 4-hour duration, i.e., 06:00-10:00 (Period I), 10:00-14:00 (Period II) and 14:00-18:00 (Period III) hours, were collected each day (sample of 06:00-10:00 on 16/11/2019 is not included). An average of 821 (total n=8210) agricultural residue burning events (mainly of rice crop, a C3 plant) were reported during the campaign period from the neighbouring regions (Punjab, Haryana and Uttar Pradesh) of Delhi. A HYSPLIT air mass trajectory showed the transport of air parcels during this period over Delhi from these regions indicating biomass burning to be a prominent source of aerosols.

We found an average $PM_{2.5}$ concentration of 372±182, 257±146 and 183±129 $\mu g\ m^{-3}$ during Periods I, II and III, respectively. The organic carbon (OC)/elemental carbon (EC) ratios were observed as 6.9±2.8, 7.2±2.1 and 6.6±1.6 in Periods I, II and III, respectively, which are characteristic of biomass burning and are similar to the previously reported values from New Delhi urban sites (5±1) in winter (Kumar *et al.*, 2015). We observed consistently low ratios of water-soluble OC (WSOC)/OC during all three time-periods (0.5±0.0 (Period I), 0.5±0.1 (II), 0.6±0.1 (III)), indicating a fresh particle emission. The lower WSOC/OC ratios indicate a minimal photochemical aging of aerosols.

The average nitrogen isotopic values ($\delta^{15}N$) of total nitrogen (TN) ranged from 15.5±2.1‰ to 18.7±1.2‰ throughout the day with higher values during Period I, indicating the burning of agricultural residue. The $\delta^{15}N$ values were similar to those reported from burning of C3 plant (2.0 to 19.5‰) and biofuel/biomass burning influenced aerosols (21.3±1.8 ‰) in Mumbai. The lower WSOC/OC ratios together with $\delta^{15}N$ suggest that the influence of agricultural residue burning is significant on the air quality of the city. The higher values of all the markers and $PM_{2.5}$ mass concentrations during the early morning suggest the fresh emission during Period I or at night (nighttime residue burning is a usual practice in the region). The average $\delta^{13}C$ of total carbon (TC) ranged from -27.0±0.8‰ to -26.3±0.3‰, again indicating the burning of C3 plant materials. Similar values have been reported in Singapore from a large scale C3 forest fire of Indonesia.

We also detected dicarboxylic acids, oxocarboxylic acids and α-dicarbonyls in the samples with a total concentration of 4130 ng m^{-3}, 379 ng m^{-3} and 40.6 ng m^{-3}, respectively. Oxalic acid was found to be the most abundant diacid (2370±1200 ng m^{-3} (I), 2050±1090 ng m^{-3} (II), 1930±1200 ng m^{-3} (III)) followed by succinic acid (1020±701 ng m^{-3} (I), 671±448 ng m^{-3} (II), 516±413 ng m^{-3} (III)) with higher levels during Period I in all the samples. Similarly, pyruvic acid (174±39 ng m^{-3} (I)) was the most abundant

oxocarboxylic acid followed by glyoxylic acid (102±47 ng m^{-3} (I)). The ionic analysis showed the presence of F^-, MSA^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Ca^{2+}, with the dominant anion of SO_4^{2-} (16.4±12.9 ng m^{-3}) followed by Cl^- (15.8±18.1 ng m^{-3}) and the dominant cation of NH_4^+ (18.3±14.3 ng m^{-3}) followed by K^+ (2.1±1.6 ng m^{-3}).

This study demonstrated that a field burning of agricultural residues (C3 plant) is the important source causing high levels of organic and inorganic pollutants (aerosols) in Delhi after the harvest season (November).

